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14. ABSTRACT In this exploratory project, we explored the hypothesis that macroscopic deformation of an elastomeric support could result in molecular deformation of embedded, stress-bearing catalysts and influence their reactivity. The focus was on the selectivity of hydroformylation for branched to linear aldehydes from terminal olefins. We succeeded in creating new, heterogeneous supports with active, stress-bearing catalytic sites. To date, we have not been able to prove our second hypothesis, that mechanically deformed catalysts within the network have altered					
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Report Title

Harnessing Macroscopic Forces in Catalysis

ABSTRACT

In this exploratory project, we explored the hypothesis that macroscopic deformation of an elastomeric support could result in molecular deformation of embedded, stress-bearing catalysts and influence their reactivity. The focus was on the selectivity of hydroformylation for branched to linear aldehydes from terminal olefins. We succeeded in creating new, heterogeneous supports with active, stress-bearing catalytic sites. To date, we have not been able to prove our second hypothesis, that mechanically deformed catalysts within the network have altered reactivity. Work in the latter area is still ongoing subsequent to the end of the ARO funding.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Number of Papers published in peer-reviewed journals: 0.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

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Peer-Reviewed Conference Proceeding publications (other than abstracts):

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Number of Manuscripts: 0.00

Number of Inventions:

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NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Nick Perch	1.00
FTE Equivalent:	1.00
Total Number:	1

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Stephen Craig	0.00	No
Ross Widenhoefer	0.00	No
FTE Equivalent:	0.00	
Total Number:	2	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	0.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:.....	0.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:.....	0.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):.....	0.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:	0.00

Names of Personnel receiving masters degrees

<u>NAME</u>
Total Number:

Names of personnel receiving PHDs

<u>NAME</u>
Total Number:

Names of other research staff

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	
Sasa Korom	0.50	No
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Final Project Report
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Statement of the Problem Studied

Chemical reactions are commonly accelerated by external energy sources such as heat, light, or electric potential. Mechanical force, by comparison, is almost entirely untapped as a reaction input, despite its ability to induce reactions that are effectively impossible to obtain by conventional methods. It has long been established, for example, that physically snapping a piece of poly(ethylene) plastic involves homolytic carbon-carbon bond scission—a chemical reaction whose activation energy of ca. 90 kcal mol⁻¹ makes it more difficult than almost any potentially useful chemical transformation.¹⁻¹³ More recently, Hickenboth and co-workers reported that mechanical force induces an intramolecular rearrangement to give the product that would result from a symmetry-forbidden electrocyclic ring opening.¹⁴

While the spectacular potential of mechanically driven reactivity has been demonstrated in stoichiometric reactivity, mechanical force-induced catalysis (“mechanocatalysis”) has yet to be demonstrated. If shown to be viable, mechanocatalysis would create a new avenue by which to approach chemical transformations—the manipulation of catalyst stress state—an avenue that complements traditional routes of optimizing catalyst structure or loading, temperature, pressure, solvent, etc...

The promise of mechanocatalysis comes from a powerful combination of attributes: the magnitude of macroscopic forces relative to interatomic and intermolecular forces, and the potential to apply mechanical energy specifically and directionally to the bonds of interest. Thus, the potential to influence not only the rates of reactions, but the selectivity for specific reaction outcomes, is fundamentally different from that which exists as a function of temperature. To be useful in practical chemical synthesis, the power of mechanically driven reactivity needs to be expanded beyond a single reaction within a high molecular weight polymer and into the realm of catalysis.

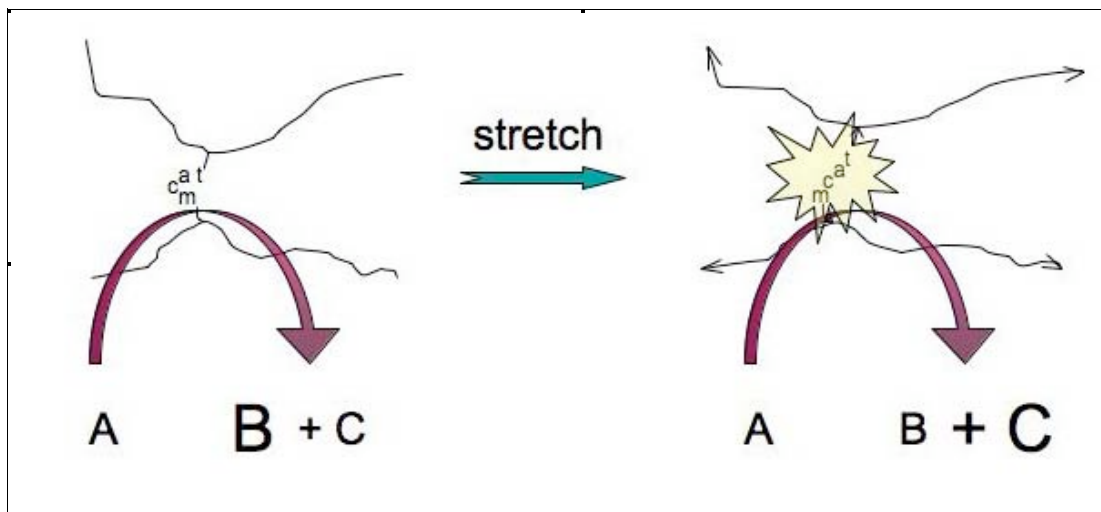


Figure 1. Schematic representation of biasing reaction selectivity via mechanocatalysis. A catalyst, “mcat”, is embedded in an elastomeric support. Deformation of the elastomeric support transfers mechanical stress to mcat. Under stress-free conditions, mcat catalyzes the transformation of reactant A into a mixture of major product B and minor product C. Deformation of the mechanocatalyst preferentially populates an extended conformation of the catalyst, and switches the reaction selectivity toward C as the major product.

We pursued here the first synthetic, mechanically responsive catalyst. Since this work began, Sijbesma¹⁵ has reported the mechanical *activation* of latent catalysts, but the reactions enabled by those catalysts, once activated, were identical to those of the same pre-catalysts activated by other means. Our goal was (and remains) to not activate, but *modulate*, the activity of a mechanocatalyst. Our Specific Aims were:

Specific Aim 1. Synthesize elastomeric organogels and bulk rubbers with embedded, stress-bearing catalytic sites.

Specific Aim 2. Demonstrate catalytic competence of stress-bearing catalytic sites.

Specific Aim 3. Maximize the stress-dependence of the selectivity in catalytic reactions. Our goal for this initial project phase is to demonstrate a mechanical bias that results in a measurable change in *n:i* selectivity.

Summary of Important Results

We successfully completed Aims 1 and 2. We adapted our original research plan away from bis(phosphine) ligands, because their synthesis and isolation was found to be incompatible with a short-term discovery project. Instead, we developed a robust set of Rh catalysts based on bis(*N*-heterocycliccarbene) (NHC) ligands. These catalysts are shown in Figure 2. We synthesized swollen elastomeric organogels in which these catalysts serve as stress-bearing cross-links, and demonstrated their unperturbed activity in the swollen gels.

We have also successfully strained the gels in two ways: (1) application of an external compressive force (squashing between parallel plates), and (2) swelling by solvent. In both cases, we have yet to demonstrate a statistically significant change in activity with applied strain. Our hypothesis is that the critical limiting factor is that of heterogeneity within the support – while some of the catalysts are strained to the point that their activity is modulated, these are only a small fraction of the total catalyst population, and so the effect on the observable net activity is negligible.

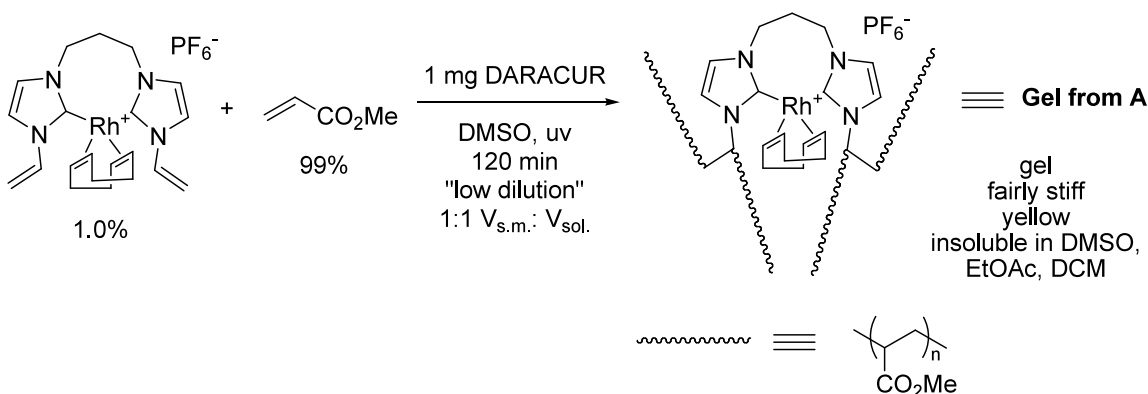


Figure 2. A (bis-NHC)Rh complex **A** (left) and its incorporation into a polyacrylate gel. The Rh complex is catalytically active within the gel, where it also acts as a stress-bearing cross-link.

In ongoing work, we are now partnering with collaborators at Carnegie Mellon and UNC to introduce molecular stress uniformly by isolating catalytic sites along the backbone of internally strained, sterically congested macromolecules such as polymer bottlebrushes.¹⁶ The internal force can be tuned directly through the molecular weight of the bottlebrush architecture, up to forces at which homolytic carbon-carbon bond scission occurs, and will provide an unambiguous test of our ultimate hypothesis.

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Appendices -- none